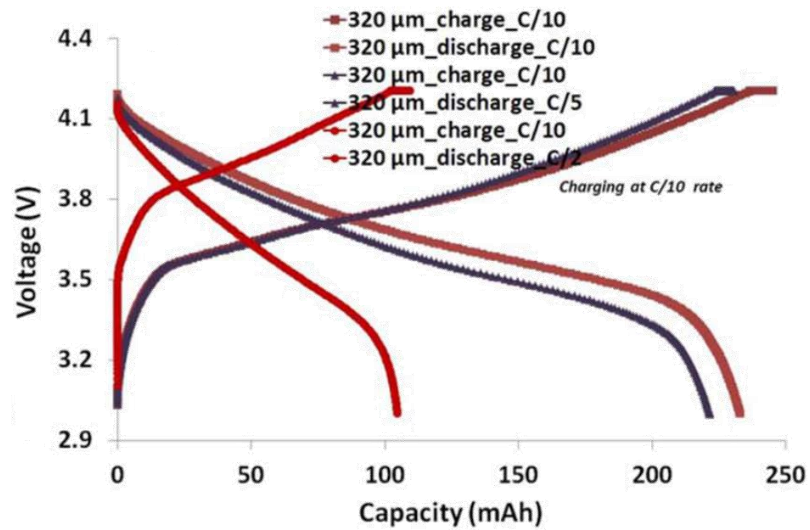
ModVal 14, 03/02/2017, Karlsruhe

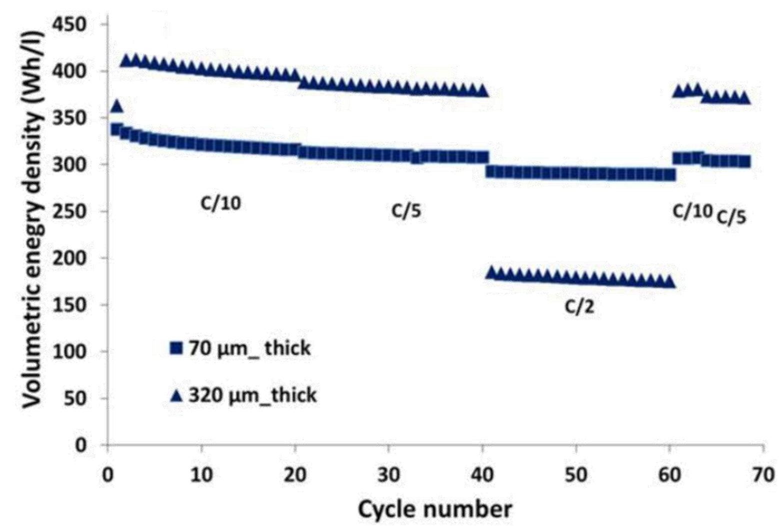
Thick electrodes for Li-Ion batteries: A model based analysis

Timo Danner, Simon Hein, Daniel Westhoff,
Volker Schmidt and Arnulf Latz

Content

Thick Li-Ion batteries?





Advantages:

- Reduction of inactive materials & production time
  → Lower cost & improved energy density

Challenges:

- Long transport pathways
  → Low rate capability & degradation

M. Singh *et al.*, *J. Electrochem. Soc.*, 162(7): A1196–A1201, 2015.

- Thermodynamically consistent multiphysics model

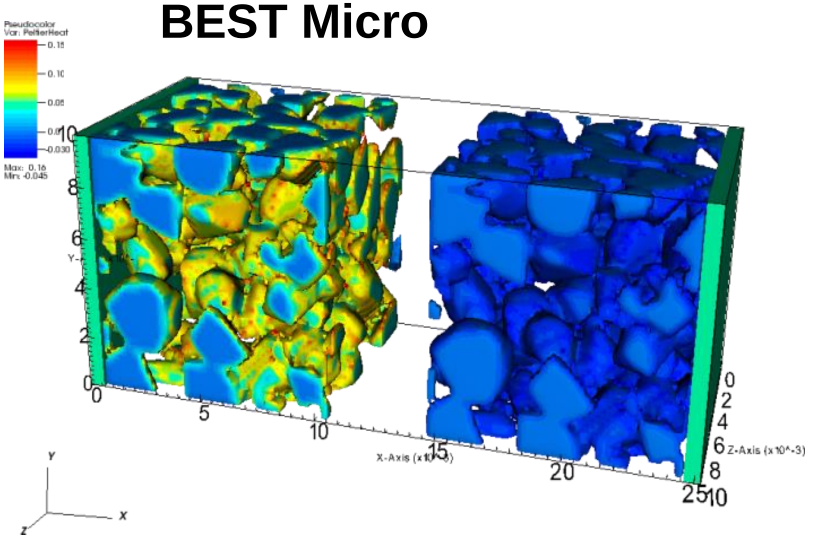
  A. Latz and J. Zausch, J. Power Sources 196, 3296 (2011)

- Finite-Volume Code based on the CoRheoS framework of Fraunhofer ITWM
  - Newton algorithm for nonlinear iterations
  - Algebraic multigrid (SAMG) for Linear Algebra

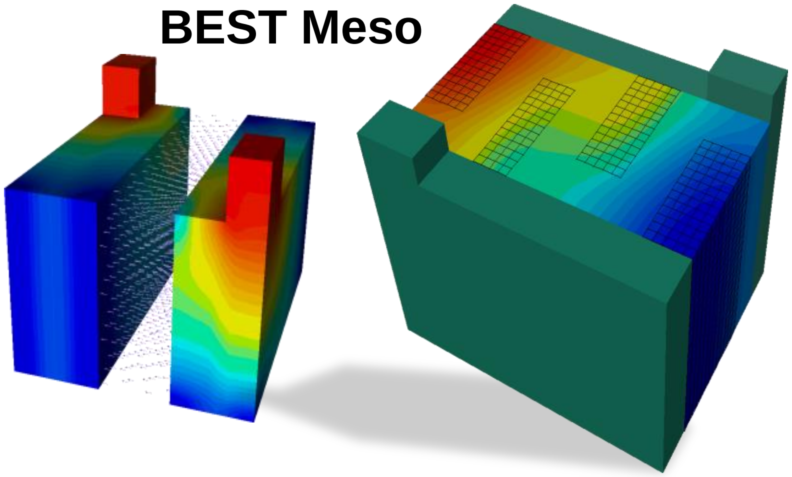
- Input: geometry and material parameters

- Output: Li-ion concentrations ***c*,** electric voltages ϕ, temperatures T in each spatial point

BEST Micro



BEST Meso

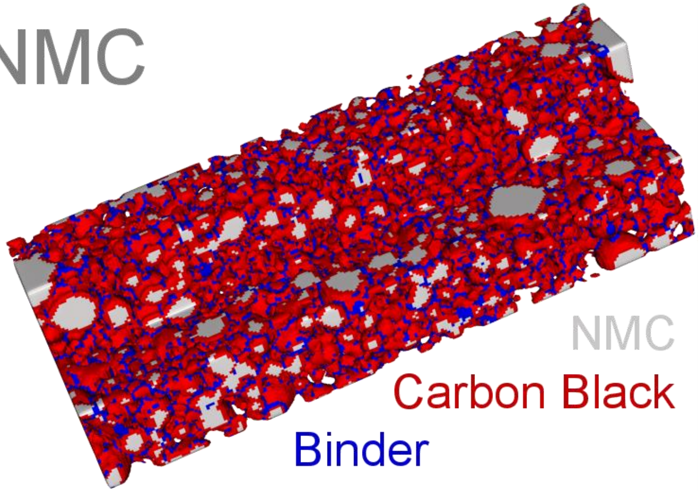


Electrode and cell geometries

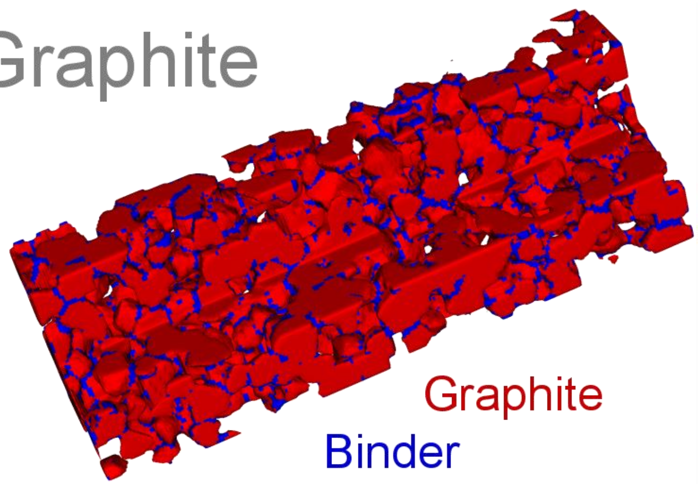
- Electrode structure based on
  - Tomography data
  - SEM images

➔ Reconstruction and structure generation in GeoDict

NMC



Graphite



	L µm	ε^0	κ^{eff} $\mathrm{S\ m^{-1}}$	a^v $\mathrm{m^{-1}}$	β
NMC-111	320	0.383	1.0	$2.35 \cdot 10^5$	2.23
Graphite	345	0.477	10.6	$1.06 \cdot 10^5$	1.85

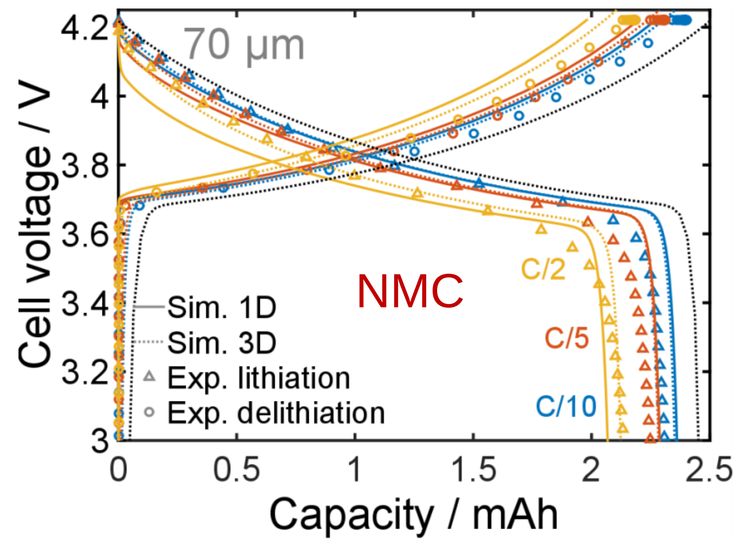
M. Ebner *et al.*, *Adv. Energy Mater.*, 3(7):845–850, 2013.

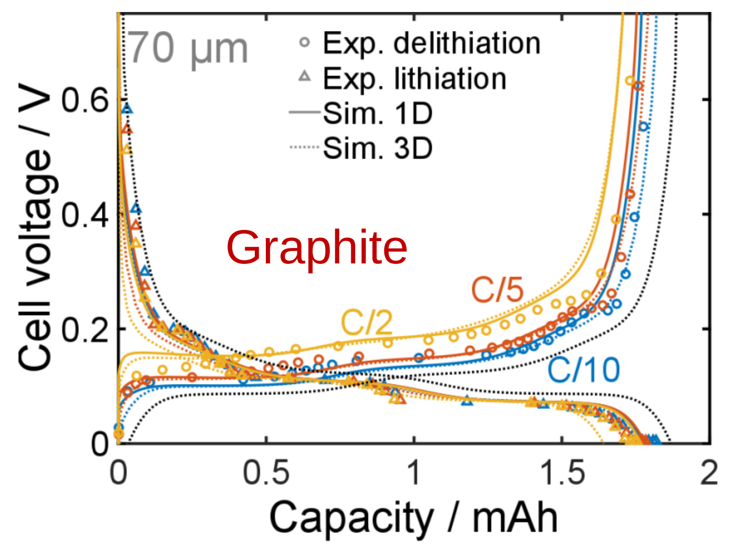
Danner, T. *et al. J. Power Sources* **334,** 191–201 (2016).

Model parameterization…

- Parameters from
  - Literature
    (κ, t_{Li^+}, D_e, D_s, …)
  - Geometry
    (L, A , ε_0, ε_NMC, $\varepsilon_\mathrm{Binder}$, …)
  - Dedicated experiments
    (OCV, σ^eff)
  - Fit to half-cell data (1+1D)
    (i_{00})

➔ Agreement of 3D simulations with experimental data





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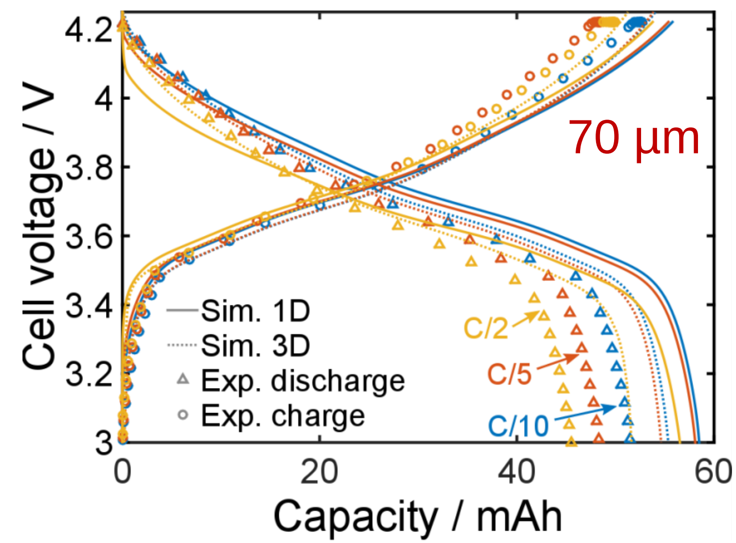
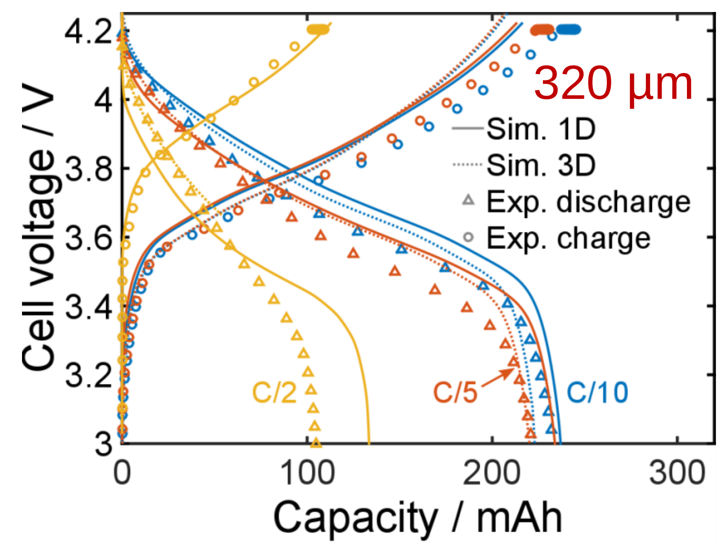
… and validation

- Deviation Exp. ↔ Sim.
  - NMC
    - ➔Production process? (Inhomogeneous CB and/or binder distribution)
  - Graphite
    - ➔Li plating?
    - ➔Electrode structure?

➔ Good qualitative agreement!





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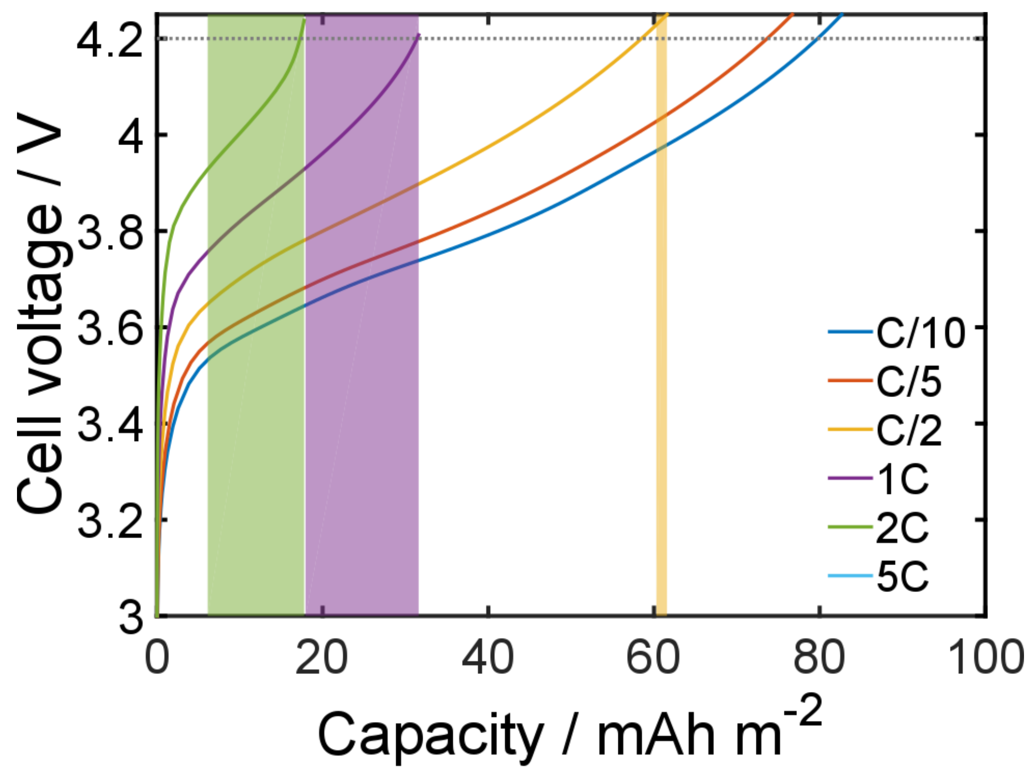
Lithium plating?

Thermodynamic condition:

$$\eta = \phi_{elode} - \varphi_{elyte}$$
$$= \Delta\phi < 0$$

- Effect of current density
  - Small current
    ➔No plating
  - High current
    ➔Condition met



➔ Where does plating occur?

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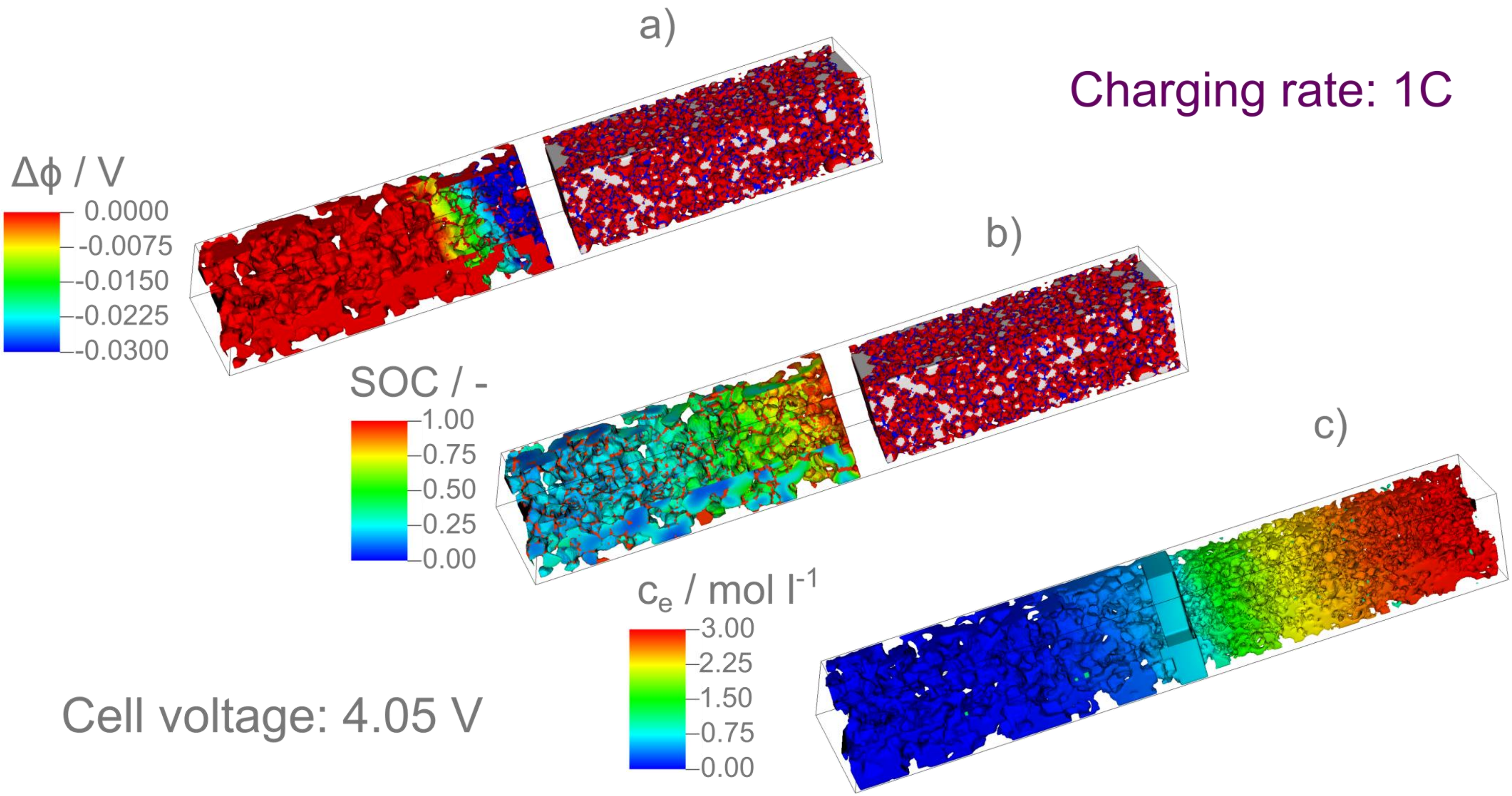
Lithium plating?

Thermodynamic condition: $\Delta\phi < 0$

Charging rate: 1C



Cell voltage: 4.05 V

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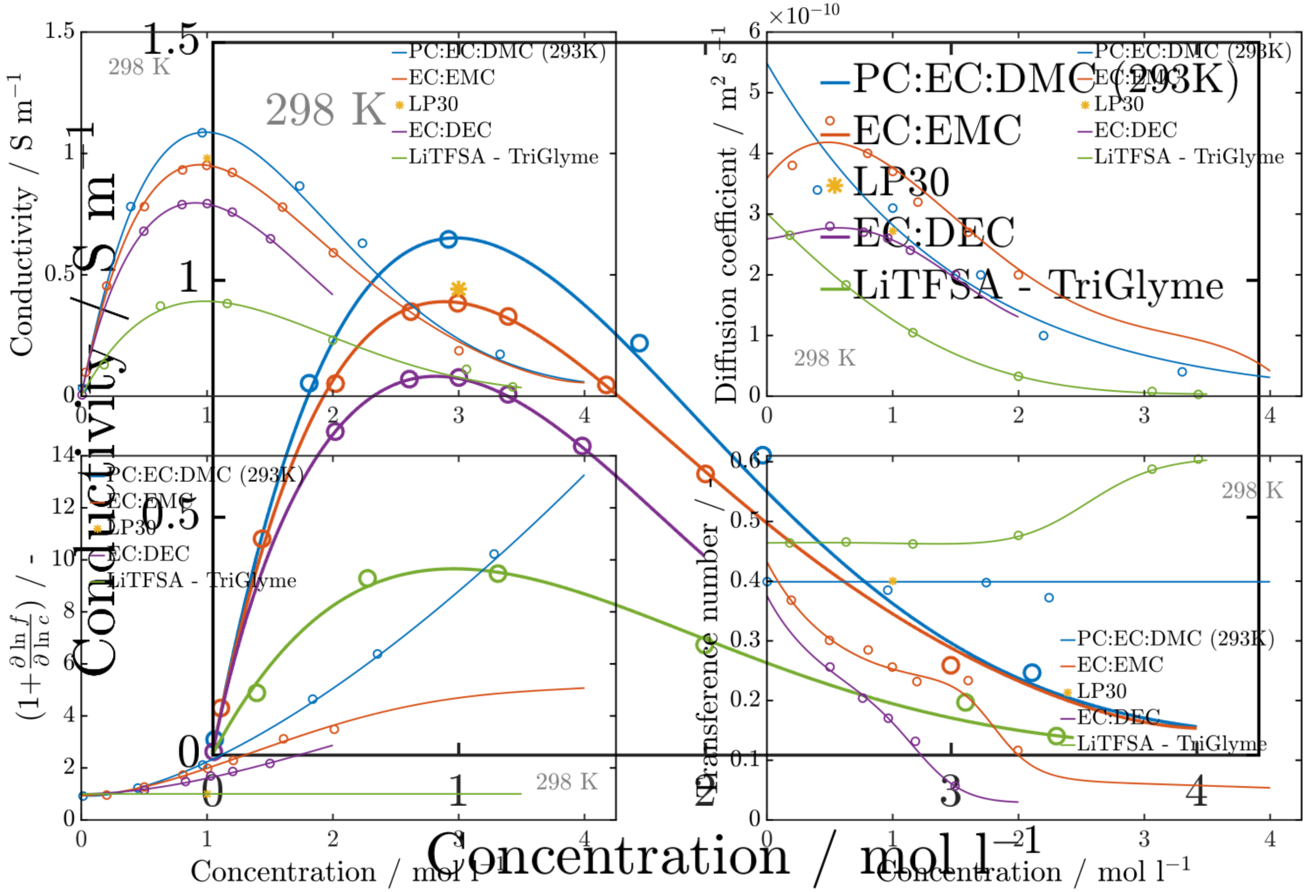
Li+ transport parameters

- Parameters
  - Conductivity
  - Diffusion coefficient
  - Transference number
  - ‚Thermodynamic factor‘

➔ Concentration (and temperature) dependent parameters needed

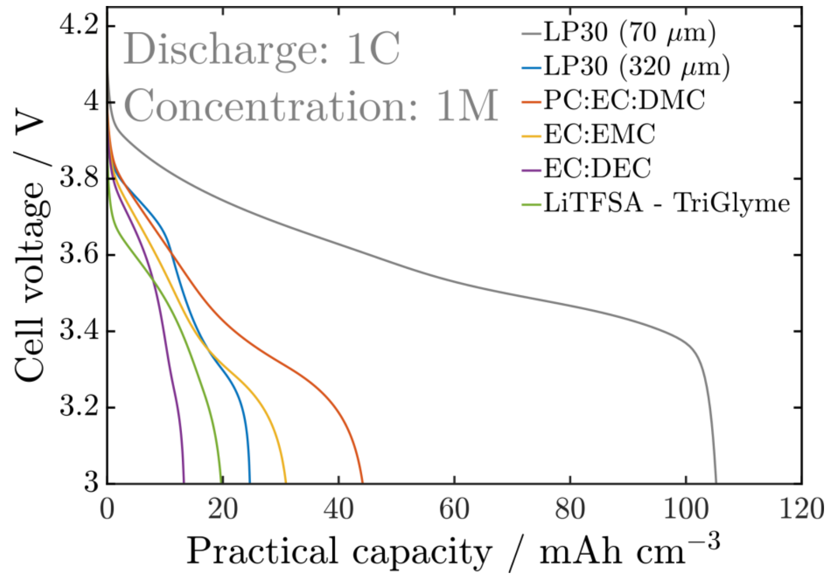


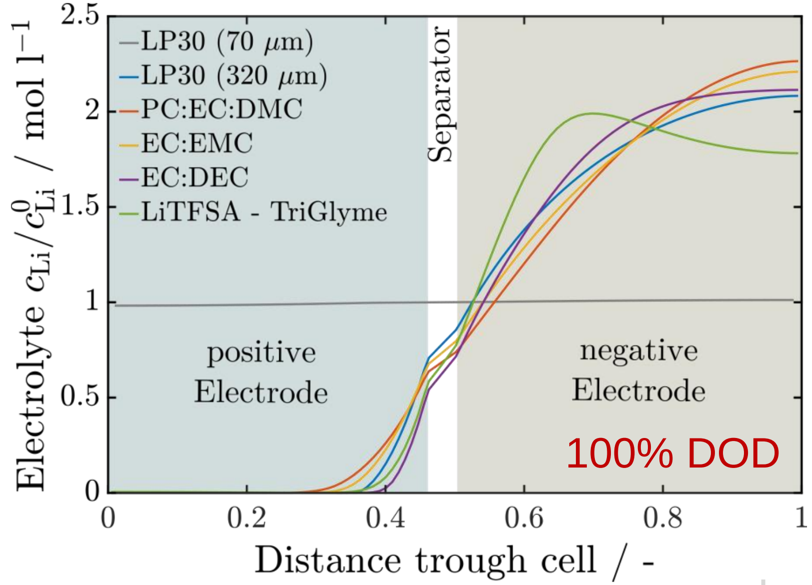
Valoen, L. O. *et al., J. Electrochem. Soc.* **152,** A882 (2005).
Nyman, A. *et al.*, *Electrochim. Acta* **53,** 6356–6365 (2008).
Zhang, C. *et al.*, *J. Phys. Chem. B* **118,** 5144–5153 (2014).
Weirather-Köstner, Wachtler, ZSW, (2017)
Lundgren, H. *et al.*, *J. Electrochem. Soc.* **162,** A1334–A1340 (2015).
Djian, D. *et al.*, *J. Power Sources* **187,** 575–580 (2009).
Lundgren, H. *et al.*, *J. Electrochem. Soc.* **162,** A413–A420 (2015).

Reference: 1M & 1C

- 70 µm electrodes (benchmark)
  - ➔ Sufficient supply of Li
- Thick electrodes
  - ➔ Li depletion in cathode
- Fast transport in PC:EC:DMC
  - ➔ Highest capacity

➔ How to increase the electrode utilization?





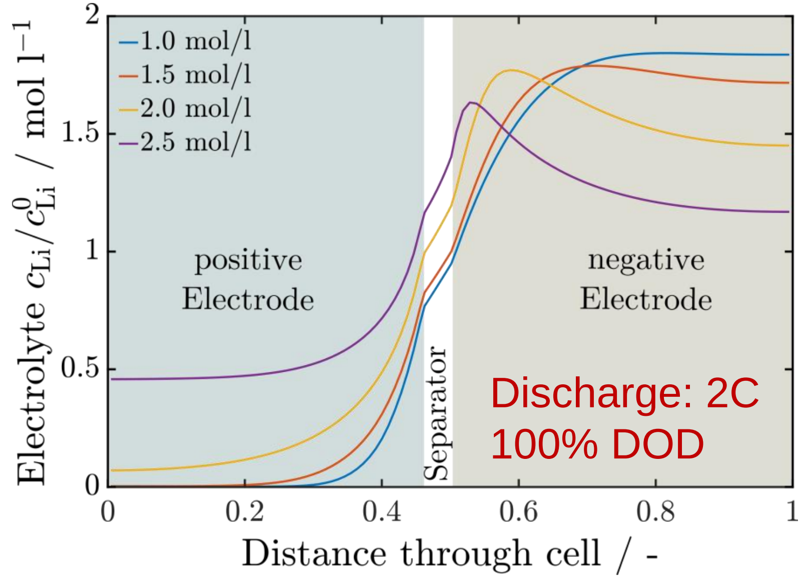
PC:EC:DMC – 2C

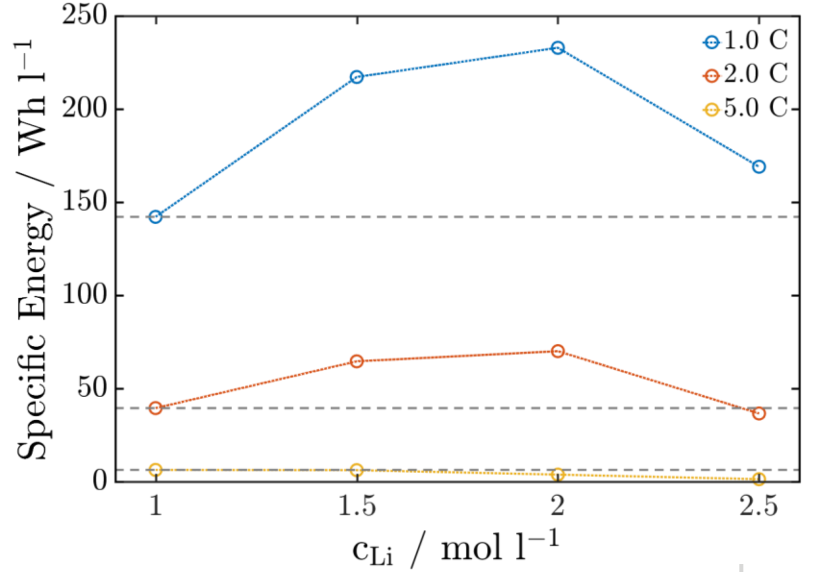
- High concentrations
  - Sufficient supply of Li

  ➔ Improved electrode utilization
  - Increase of ohmic losses

  ➔ Cut-off @ lower capacity

➔ Maximum capacity at intermediate concentrations





HighEnergy

➔ Design and processing of thick electrodes

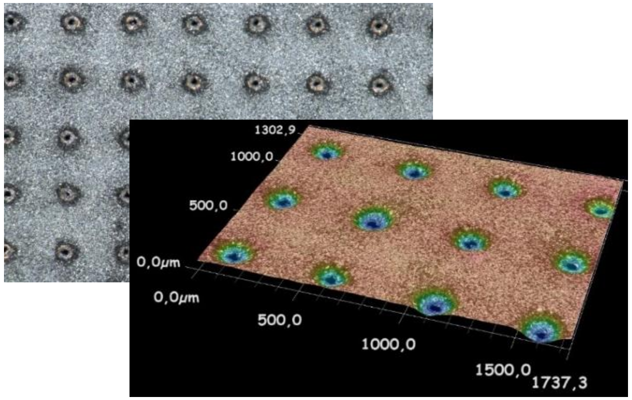
- From material…

(active material, binder, additives)

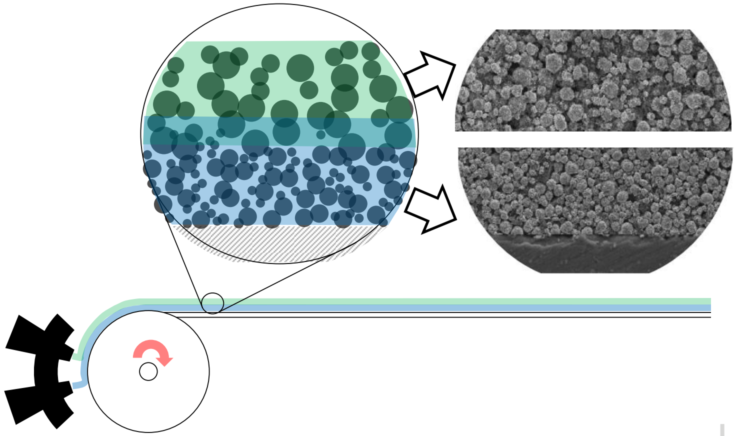
- …to cell level

(coating, structuring, stapling)

Laser-Perforation

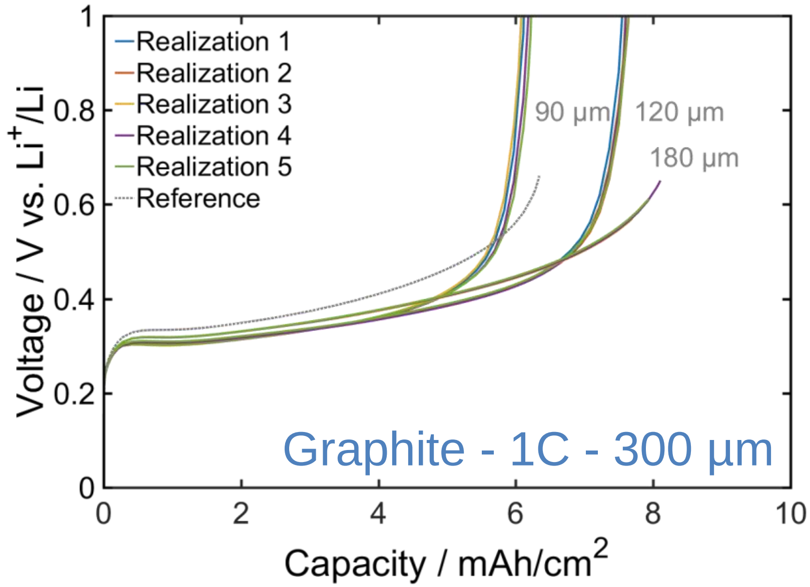


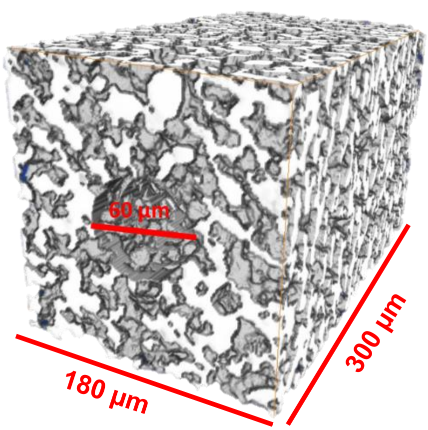
Layered electrodes



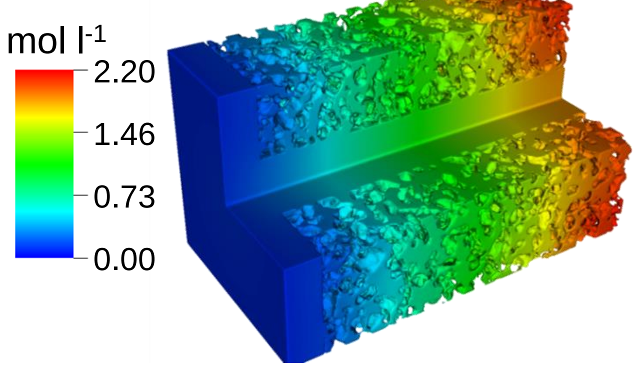
Example: Laser-Perforation

- Design parameters:
  - Thickness (300 µm)
  - Diameter (60 µm)
  - Distance (90 / 120 / 180 µm)
- Goal: Optimization of ion transport





Electrolyte



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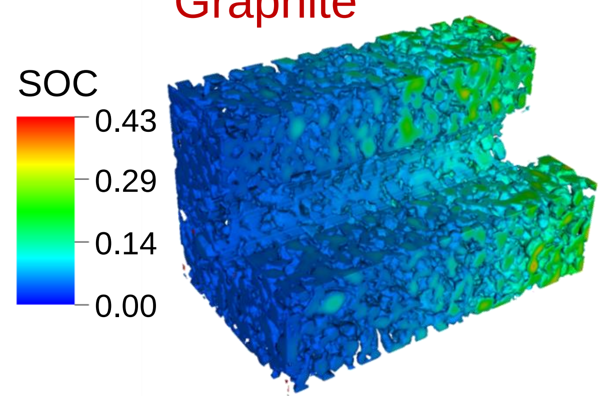


D. Westhoff *et al. Comput Mater Sci*, 126, 453–467 (2017)

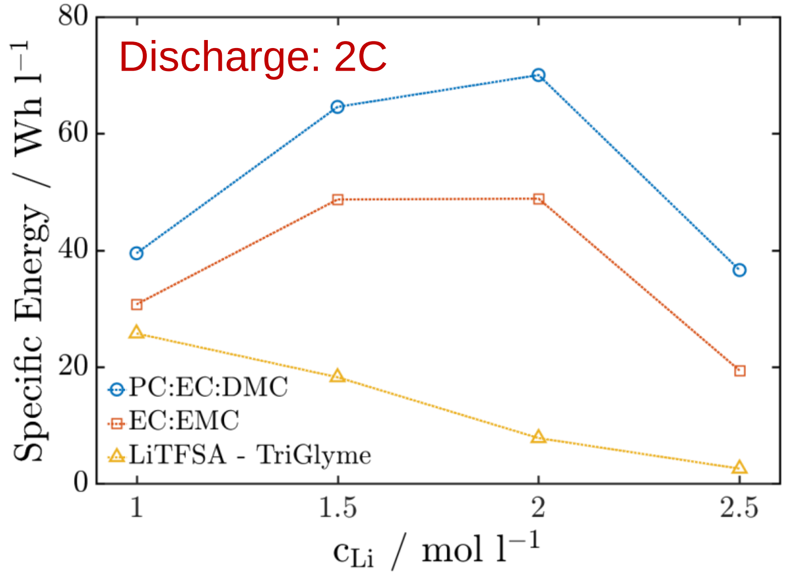
- BEST – Battery Electrochemistry Simulation Tool
  - ➔ Microstructure-resolved simulations on cell level
- Thick electrodes
  - Electrode structure from tomography data & stochastic models
  - Validated model for qualitative predictions
- Li plating?
  - ➔ Tendency to dendrite formation at high C-rates
- Highly concentrated electrolytes
  - ➔ Improved energy density
- Structuring of electrodes
  - ➔ Laser-Perforation improves ion transport

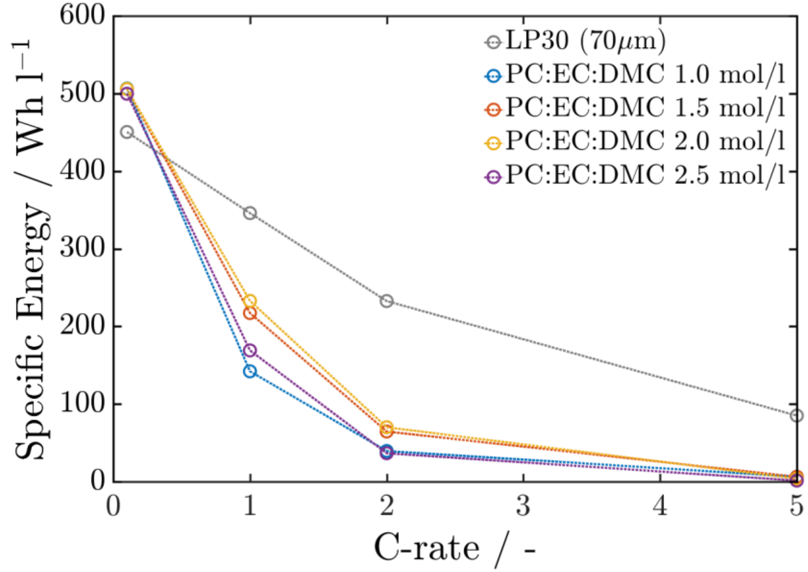
Thank you for your attention!

Specific energy

- Specific energy @ 2C
  - Similar for EC:EMC
  - Decrease for TriGlyme
  - ➔General behavior?
- Benchmark:
  - ➔Low C-rate: Thick electrode
  - ➔High C-rate: Thin electrode

➔ Additional improvements needed!



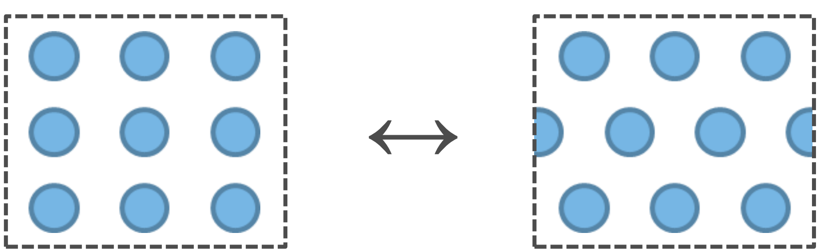


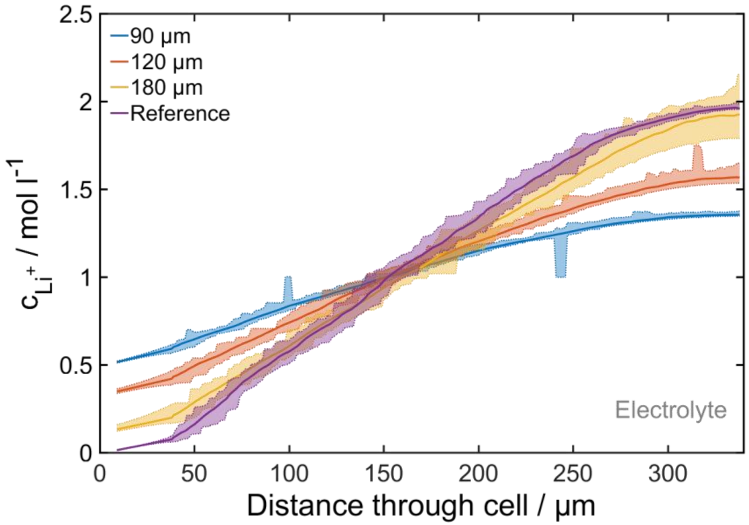
Example: Laser-Perforation

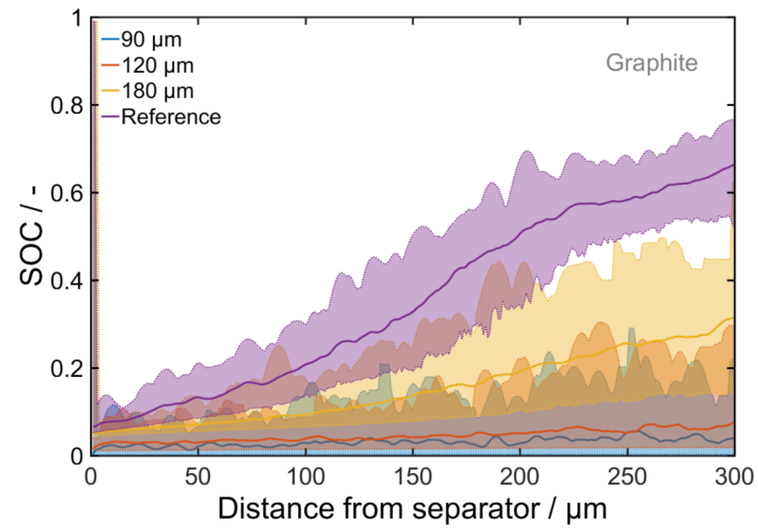
➔ Improved ion transport

- Whole distance ↑
  - c_{Li^+} gradient ↑
  - graphite utilization ↓
  - deviation from mean value ↑

➔‘face centered‘ arrangement of laser wholes







BEST Micro

➔ Resolution of electrode micro-structure

- Transport in electrolyte

$$0 = \frac{\partial c_e}{\partial t} + \vec{\nabla} \cdot \underbrace{\left[-D_e \vec{\nabla} c_e + \frac{t_+ \vec{j}_e}{F} \right]}_{\vec{N}_e}$$

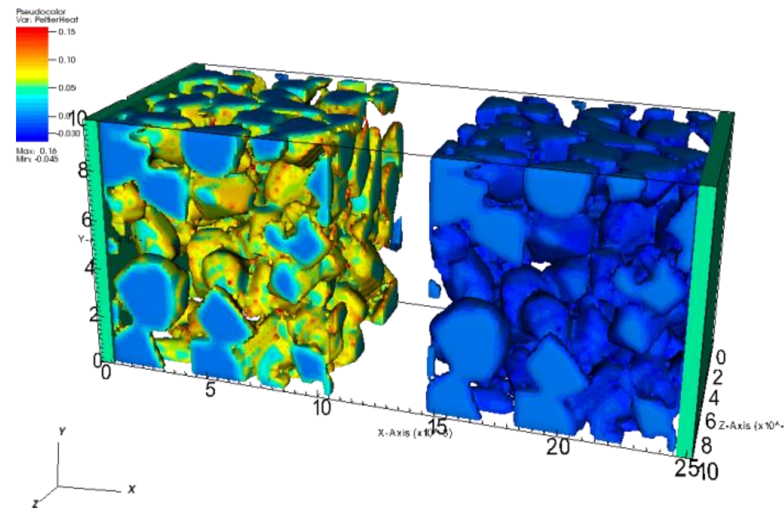
$$0 = \vec{\nabla} \cdot \underbrace{\left[-\kappa_e \vec{\nabla} \Phi_e + \frac{\kappa_e (1 - t_+) R T}{F} \vec{\nabla} \ln c_e \right]}_{\vec{j}_e}$$

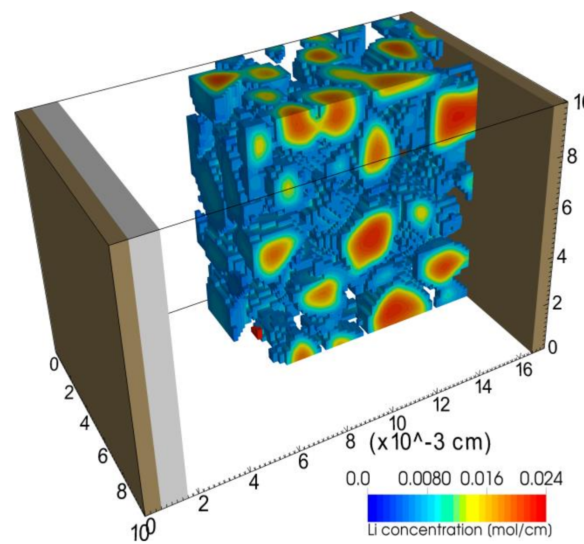
- Transport in active particles

$$0 = \frac{\partial c_s}{\partial t} + \vec{\nabla} \cdot \underbrace{\left[-D_s \vec{\nabla} c_s \right]}_{\vec{N}_s}$$

$$0 = \vec{\nabla} \cdot \underbrace{\left[-\kappa_s \vec{\nabla} \Phi_s \right]}_{\vec{j}_s}$$

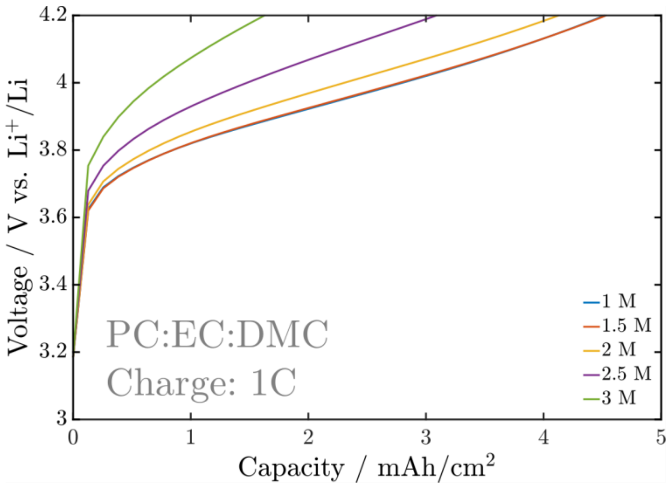
➔Simulation on cell level

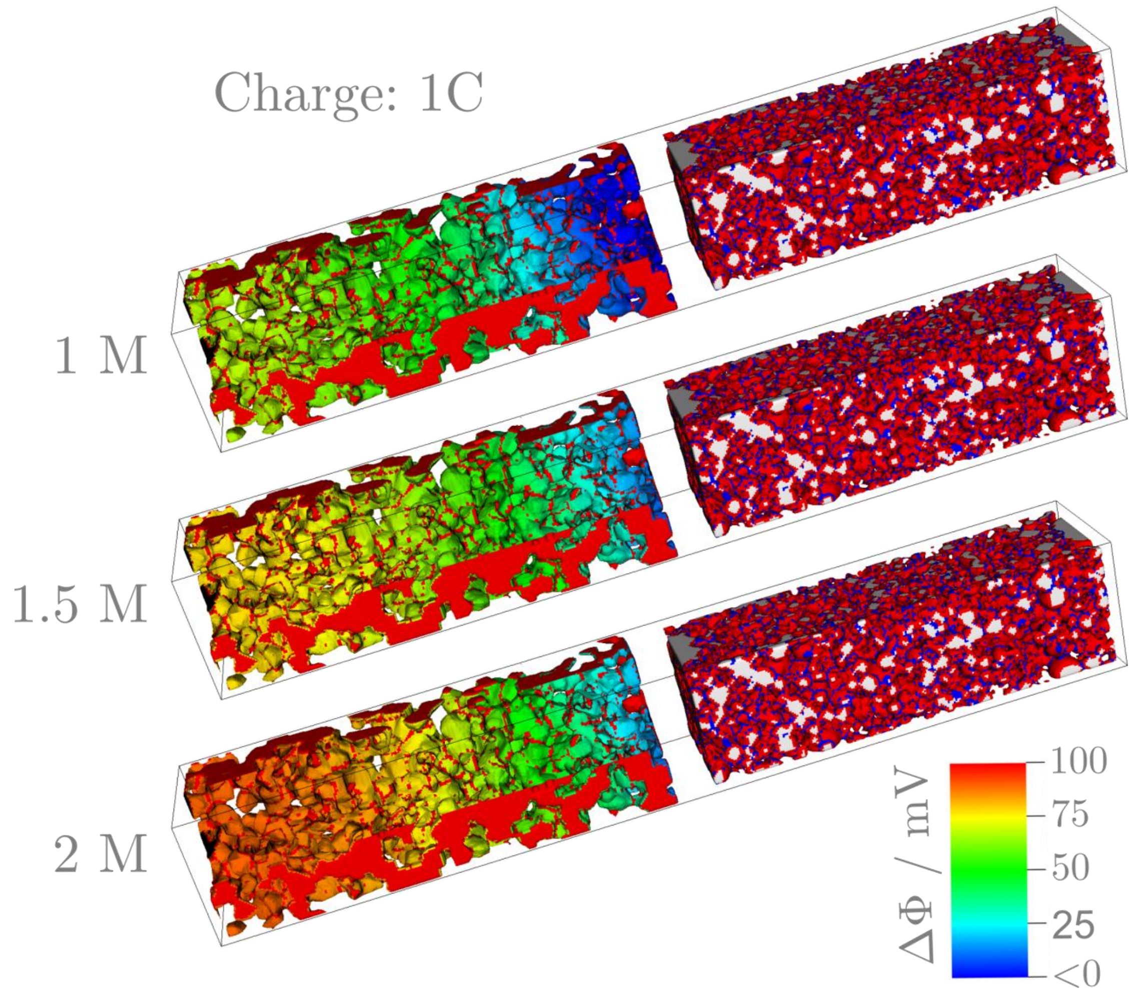




Li plating?

- Influence of
  - Position
  - Size
- Small defect
  - No effect

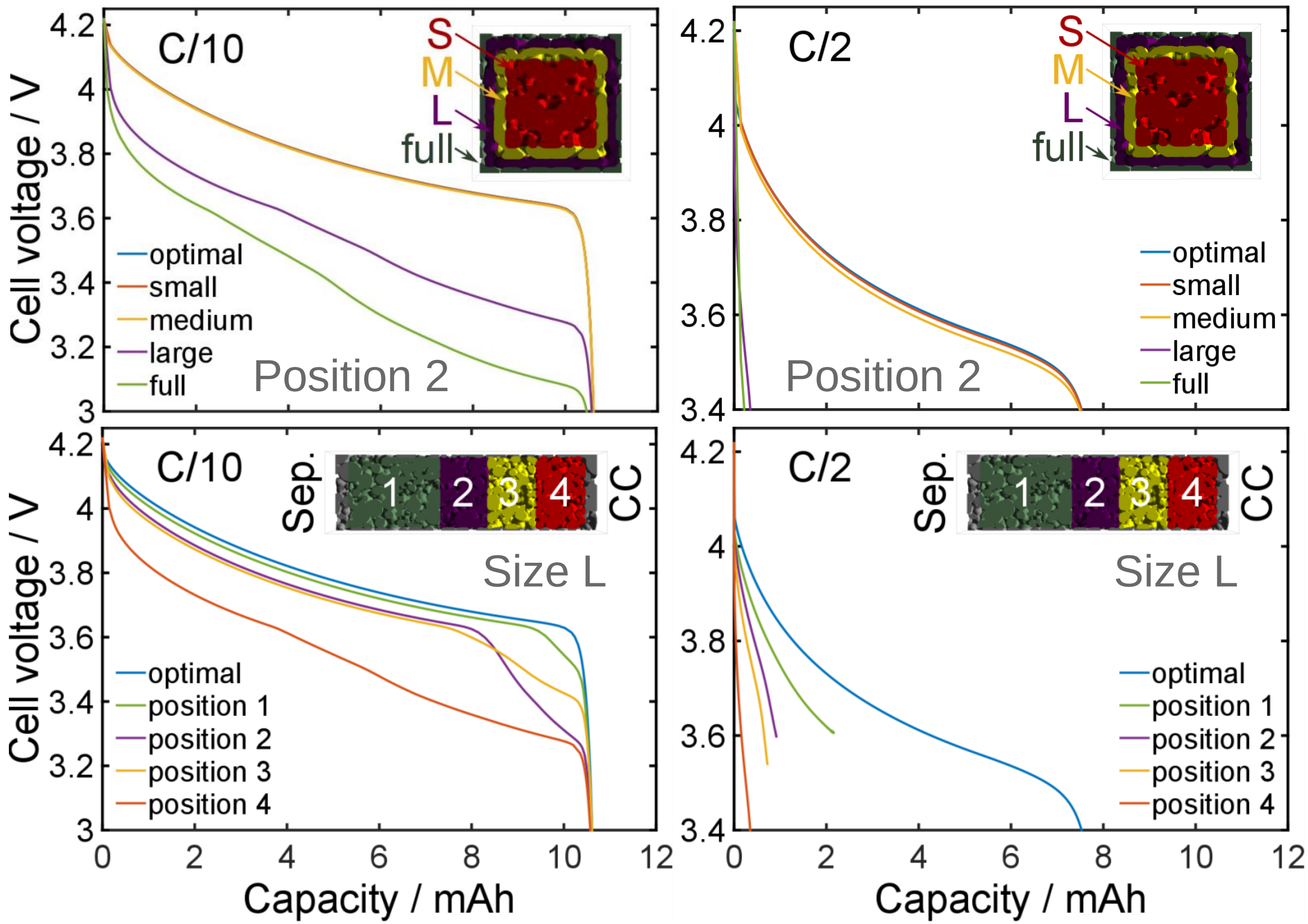




Carbon black distribution?

- Influence of
  - Position
  - Size
- Small defect
  - No effect
- Large defect
  - Overpotential
  - Capacity loss

➔ Origin of stages?



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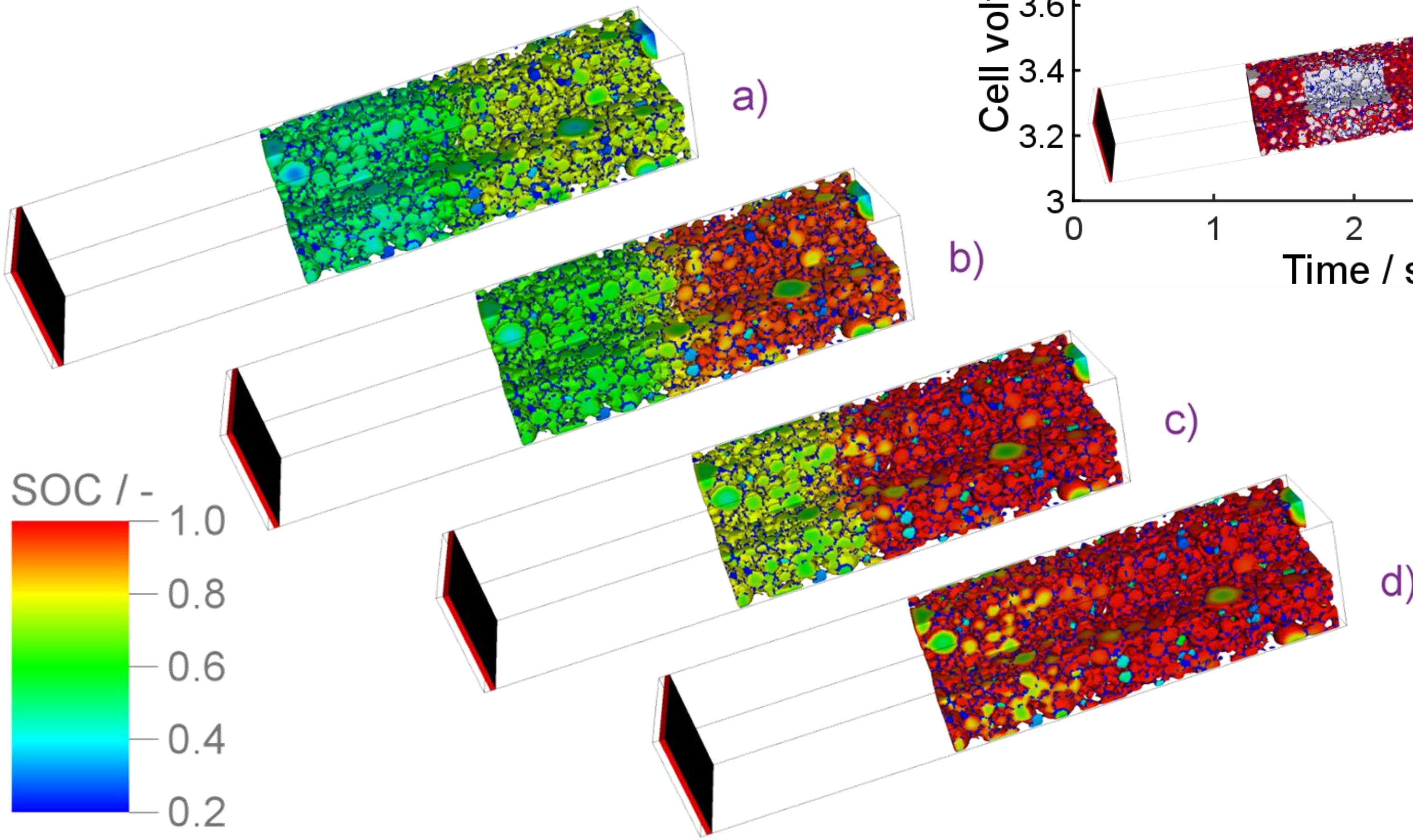
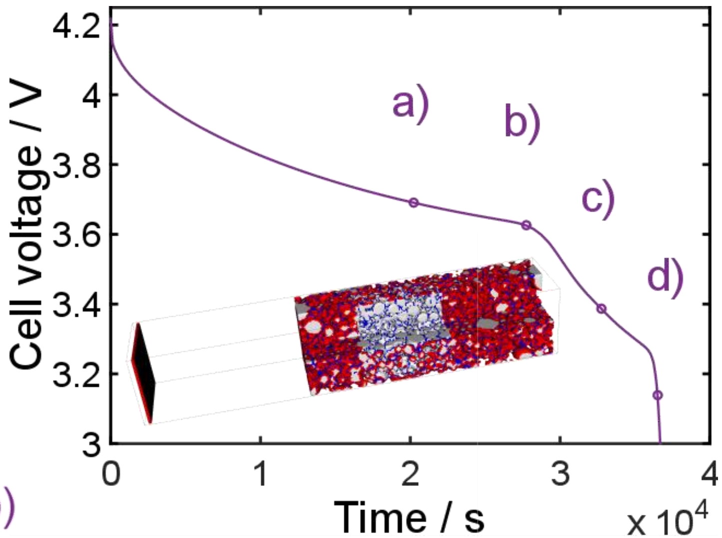
Carbon black distribution?





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- Batteries:
  - HIU Ulm

- Center of Excellence for research in electrochemical energy storage
- Founded in Jan. 2011
- New building on University Ulm campus for 100++ scientists (October 2014)